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Melzer, C.; Krasnikov, V. V.; Hadziioannou, G.

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Organic donor/acceptor photovoltaics: The role of C_{60}/metal interfaces

Christian Melzer and Victor V. Krasnikov[a)]
Department of Polymer Chemistry, Material Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Georges Hadziioannou[b)]
Ecole Européenne Chimie Polymères Matériaux (ECPM), University Louis Pasteur Strasbourg, 25 rue Becquerel, F-67087 Strasbourg Cedex 2, France

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The photovoltaic properties of thin films based on donor/acceptor heterojunctions, prepared by means of either consecutive evaporation or co-evaporation, and sandwiched between asymmetric contacts are investigated. (E,E,E,E)-1,4-bis[(4-styryl)styryl]-2-methoxy-5-(2′-ethylhexoxy)benzene (MEH-OPV5) and Buckminster fullerene C_{60} are employed as donor and acceptor materials, respectively. Current-voltage measurements and impedance spectroscopy on the donor and the acceptor single-layer cells suggest the presence of a strong dipole layer at the C_{60}/metal interfaces. The correlation between the photovoltaic performances and film morphologies is discussed. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1570936]

The introduction of organic semiconductors has triggered interest in the field of photodetectors[1–3] and solar cells[4–7] as devices of any shape can be produced at potentially low cost. However, efficiencies of such devices are currently much lower than those of their inorganic counterparts,[8] demanding a further search for more efficient organic materials and better understanding of the device physics.

The photovoltaic effect involves the creation of electrons and holes under optical excitation and their successive collection at opposite electrodes. In organic semiconductors, illumination creates excitons that need to dissociate into free holes and electrons, suggesting donor/acceptor-type of photovoltaic systems.[4,5,9] Currently, two basic donor/acceptor device structures are discussed. Double-layer device structures with a single planar heterojunction interface show good diode behavior, but the limited exciton dissociation interface causes a rather low sensitivity. In this respect, a percolated system of donor and acceptor phases, that is, a network of heterojunctions through the entire film, seems to be more promising. In such blended structures, however, disorder might limit the photovoltaic performance. Moreover, new interfaces appear that can strongly affect the device characteristics. In this letter, we reveal the impact of the interfaces in a donor/acceptor photovoltaic cell on the device performance by investigating single-layer, double-layer, and blended photovoltaic systems of the donor (E,E,E,E)-1,4-bis[(4-styryl)styryl]-2-methoxy-5-(2′-ethylhexoxy)benzene (MEH-OPV5) and the acceptor C_{60}, with indium-tin-oxide/polyethylene dioxythiophene polystyrene sulfonate (ITO/PEDOT:PSS) (synthetic metal, $\phi = 5.2$ eV) as anode and Al ($\phi = 4.3$ eV) as cathode.

Organic donor/acceptor photovoltaic cells were prepared on ITO-coated glass substrates used as anode ($\phi \approx 4.7$ eV). ITO glass (Merck KGaA, $<100\ \Omega/\square$) was cleaned by a wet cleaning procedure. PEDOT:PSS was spin-coated from a water dispersion (Baytron P TP AI 4083 without modification) on cleaned ITO plates and dried under 10^{-2} Pa at 130 °C for several minutes. MEH-OPV5 and C_{60} (BuckyUSA, 99% C_{60}) films were obtained via vacuum vapor deposition at dynamic vacuum better than 2×10^{-4} Pa. Double-layer cells were obtained by successive deposition of the two compounds, whereas percolated structures were prepared by codeposition. The deposition rate for both materials where monitored with two quartz balances separately. Typically, the thickness of the active layer was between 100 and 150 nm. Aluminum was vacuum vapor deposited at 2×10^{-4} Pa.

All measurements were done under dynamic vacuum or nitrogen atmosphere using a Solatron Si 1260 impedance/gain–phase analyzer for impedance spectroscopy and a Keithley 236 source-measure unit for *IV* measurements. The cells were illuminated from the glass side with monochromatic light of 458 nm (argon-ion laser, Spectra-Physics, BeamLok 2060). *I–V* curves were taken at a light intensity I_L of around 1 mW/cm^2.

In Fig. 1, we present *I–V* curves of an ITO/PEDOT:PSS/MEH-OPV5/C_{60}/Al double-layer cell in dark and under illumination. The cell showed a photovoltaic sensitivity (S) of around 0.054 A/W and a high fill factor (FF) of 0.45. The open-circuit voltage (U_{oc}) was measured to be 0.88 V, resulting in a monochromatic power conversion efficiency of $\sim 2\%$. S was constant over a broad range in light intensity (I_L). U_{oc} saturated to almost 1 V at I_L of approximately 10 mW/cm^2. The saturated open-circuit voltage (U_{soc}) of 0.9 ± 0.1 V averaged over several samples matches the difference in ϕ of the metal electrodes which is U_{soc} predicted by a metal/insulator/metal (MIM) model. S of an ITO/PEDOT:PSS/MEH-OPV5+C_{60}/Al codeposited cell was measured to be 0.078 A/W (Fig. 1, $I_L = 1$ mW/cm^2). At low I_L (<0.1 mW/cm^2), S was about 0.1 A/W, twice higher than that of the double-layer cell. S decreased with an increase in I_L, like it was observed elsewhere.[10]

What is remarkable is that U_{oc} of the codeposited cell

a)Electronic mail: v.v.krasnikov@chem.rug.nl
b)Electronic mail: hadzii@ecpm.u-strasbg.fr

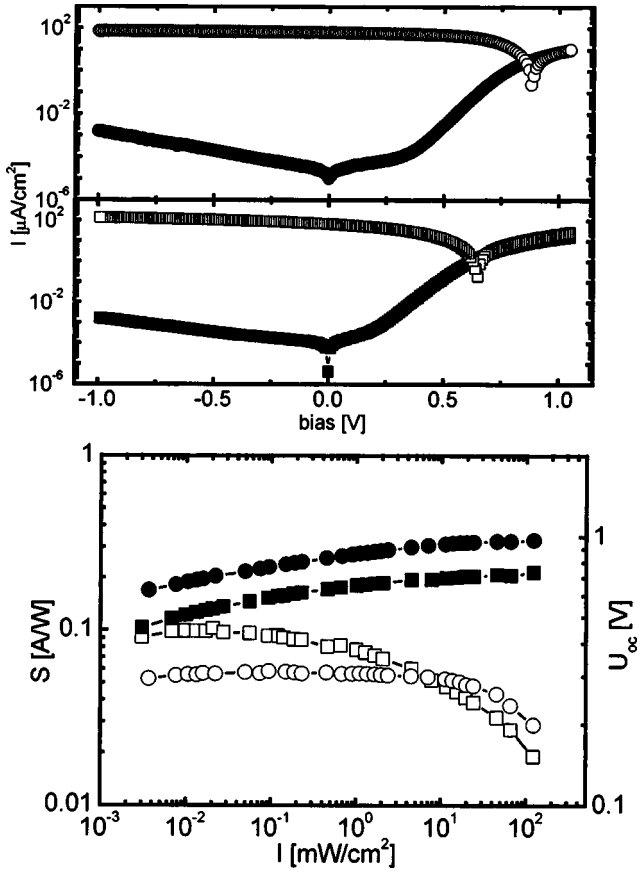

FIG. 1. Top: $I-V$ in the dark ● and under illumination ○ of a ITO/PEDOT:PSS/MEH-OPV5/C_{60}/Al double-layer cell and $I-V$ in the dark ■ and under illumination □ of a ITO/PEDOT:PSS/MEH-OPV5 $+C_{60}$/Al co-deposited cell. Bottom: The photovoltaic sensitivity ○, □ and the open-circuit voltage ●, ■ vs the light intensity for the double and co-deposited cell, respectively.

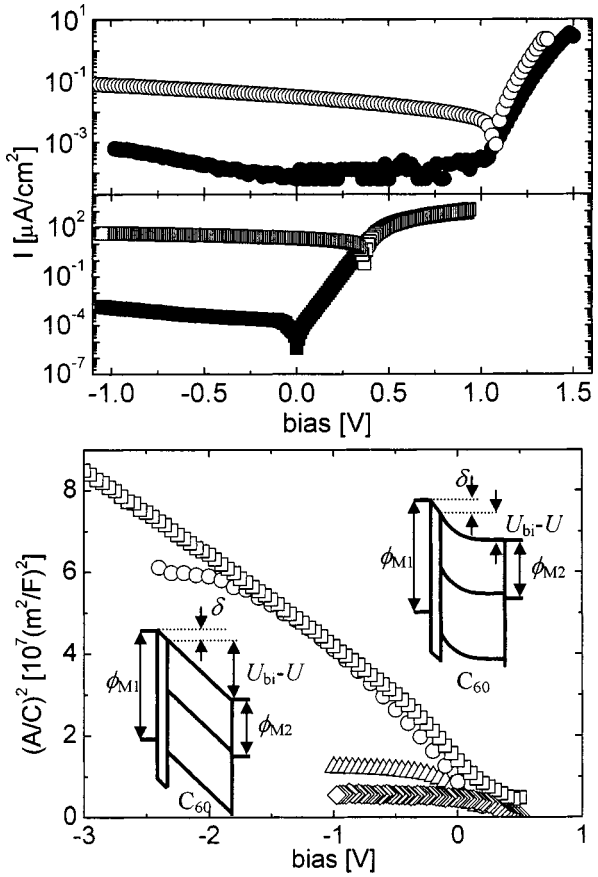

FIG. 2. Top: $I-V$ in the dark ● and under illumination ○ of a ITO/PEDOT:PSS/MEH-OPV5/Al single-layer cell and $I-V$ in the dark ■ and under illumination □ of a ITO/PEDOT:PSS/C_{60}/Al single-layer cell. Bottom: $(A/C)^2$ vs applied voltage for ITO/PEDOT:PSS/C_{60}/Al single-layer devices of 100 nm ◇, 130 nm △, 300 nm ○, and 500 nm □ thickness. The inserts show the proposed energy band diagrams.

was found to be only 0.65 V. U_{oc} saturated to 0.7 V$\pm$0.1 V averaged over several samples at high I_L, inconsistent with U_{soc} predicted by the MIM model. The same observations were reported on organic donor/acceptor photovoltaic cells of a similar system.[10] It is not clear whether the decrease of the U_{soc} from 0.9$\pm$0.1 V for the double-layer cell to 0.7 $\pm$0.1 V for the codeposited cell is due to the change of heterojunction distribution or whether other phenomena are involved. As a consequence however, the monochromatic power conversion efficiency was reduced to 1% because the increased S was compensated by the low FF and the low U_{oc}. To reveal the origin of the low U_{oc} observed in the blend we examined single-layer devices of the donor and the acceptor, respectively.

An ITO/PEDOT:PSS/MEH-OPV5/Al single-layer cell showed U_{soc} around 1.1$\pm$0.1 V (Fig. 2). In contrast, U_{soc} of an ITO/PEDOT:PSS/C_{60}/Al single-layer cell was 0.3 $\pm$0.2 V, suggesting that the C_{60} phase is responsible for the low U_{soc} of the codeposited cell. It should be noted that, unlike U_{soc} of the other cells, U_{soc} of the C_{60} single-layer cell deviated strongly from sample to sample. The most plausible causes of the low U_{soc} are interfacial dipole layers or/and interfacial surface charges[11,12] at the PEDOT:PSS/C_{60} and/or Al/C_{60} interfaces with the total strength of 0.6$\pm$0.2 V.

$C-V$ measurements on single-layer C_{60} cells showed the bias independent geometrical capacitance at high frequencies ($>$1 kHz). At low frequencies ($<$100 Hz), a steep increase of capacitance in forward bias was observed. Several models, including Schottky contact, $p-n$ junction, charging of surface states, etc., predict such bias dependant capacitance with slow dynamics. In the low-frequency regime, a linear dependence of $1/C^2$ on bias unveils a depletion capacitance and provides simultaneously its built-in potential (U_{bi}), ionized state density (N_i) and the depletion width (W) (e.g., at zero

TABLE I. Summary of the main cell characteristics.

	U_{soc} [V]	U_{bi} [eV]	N_i [10^{16} cm^{-3}]	$W_{0\,V}$ [nm]
Single-layer C_{60}	0.3$\pm$0.2	0.3$\pm$0.2	1.1$\pm$0.4	110$\pm$20
Single-layer MEH-OPV5	1.1$\pm$0.1	⋯	⋯	⋯
Double layer	0.9$\pm$0.1	⋯	⋯	⋯
Blend	0.7$\pm$0.1	0.7$\pm$0.1	0.5$\pm$0.1	240$\pm$7

bias).[11] Like the photovoltaic measurements, the $C-V$ measurements showed strong deviations of U_{bi} from sample to sample and consequently of $W_{0\,V}$ and N_i. For each cell, however, the obtained U_{bi} was close to the measured U_{soc}. $1/C^2$ versus U for a 100-nm-thick single-layer C_{60} cell was linear only in a narrow range in forward bias, whereas in reverse bias, the capacitance approached the geometrical capacitance. Film thickness increase of C_{60} extended the depletion capacitance region towards reverse bias, corroborating a transition from partly to fully depleted cell (Fig. 2) and suggesting a one-side abrupt $p-n$ heterojunction type of contact between C_{60} and one of the electrodes. Because a constant capacitance was observed over a wide range of bias and frequency for double-layer cells, the depletion layer is formed at the anode/C_{60} contact. We infer that the C_{60} layer is most likely n-doped with a rather low doping density of 10^{16} cm^{-3}. Although the origin of the doping is not known, diffusion of the top metal electrode into the bulk was reported to result in a doped organic semiconductor.[13]

We now assume that the interfacial dipole strength and the ionized state density are proportional to the corresponding material densities. Under this assumption, N_i is proportional to the density of C_{60}, and in turn the dipole strength is proportional to the surface density of the organic medium at the metal/organic interface. Since we deposited C_{60} and MEH-OPV5 in a ration of 1:1, N_i of a blended structure should be half of N_i determined for the bare C_{60} film and $W_{0\,V}$ twice longer, being confirmed by $C-V$ measurements (Table I). The dipole-layer strength in a single-layer MEH-OPV5 cell was found to be -0.2 eV. The interfacial MEH-OPV5 density in a blended cell is half of the interfacial MEH-OPV5 density of the bare MEH-OPV5 cell resulting in a dipole-layer strength of -0.1 eV at the MEH-OPV5/metal interfaces. Since the dipole-layer strength in a single-layer C_{60} cell was measured to be 0.6 eV, our assumption requires a dipole-layer contribution from the C_{60}/metal interfaces in the blend to be 0.3 eV. The predicted total dipole-layer strength in a blended cell is then 0.2 eV and the U_{soc} should be 0.7 V, in agreement with the measured value (Table I). Obviously, an additional verification of the model would require variations in the blend composition. This however, may create discontinuities of phases, resulting in a quasi double-layer structure, a situation not included in the model.

In this letter, the importance of the electrode/organic interfaces for the performance of organic donor/acceptor photovoltaic cells was demonstrated. $I-V$ and $C-V$ measurements revealed the existence of strong dipole layers at the metal/C_{60} interfaces. We demonstrated that dipole layers have a deep impact on the built-in potential and consequently on the open-circuit voltage of organic composite photovoltaic cells. The photovoltaic performance of the blended structure could be explained by a simple dilution model.

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[1] N. S. Sariciftci, D. Braun, C. Zang, V. Srdanov, A. J. Heeger, G. Stucky, and F. Wudl, Appl. Phys. Lett. **62**, 585 (1993).
[2] G. Yu, K. Pakbaz, and A. J. Heeger, Appl. Phys. Lett. **64**, 3422 (1994).
[3] G. Yu, J. Wang, J. McElvain, and A. J. Heeger, Adv. Mater. **10**, 1431 (1998).
[4] J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, and A. B. Holms, Nature (London) **376**, 498 (1995).
[5] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, Science **270**, 1789 (1995).
[6] M. Granström, K. Petritsch, A. C. Arias, A. Lux, M. R. Anderson, and R. H. Friend, Nature (London) **395**, 257 (1998).
[7] L. S. Roman, W. Mammo, L. A. A. Petterson, M. R. Andersson, and O. Inganäs, Adv. Mater. **10**, 774 (1998).
[8] A. Goetzberg and C. Hebling, Sol. Energy Mater. Sol. Cells **62**, 1 (2000).
[9] N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, Science **258**, 1474 (1992).
[10] L. Ouali, V. V. Krasnikov, U. Stalmach, and G. Hadziioannou, Adv. Mater. **11**, 1515 (1999).
[11] S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981).
[12] S. C. Veenstra, A. Heeres, G. Hadziioannou, G. A. Sawatzky, and H. T Jonkman, Appl. Phys. A: Mater. Sci. Process. **75**, 1 (2002).
[13] D. Sarkar and N. J. Halas, Appl. Phys. Lett. **63**, 2438 (1993).